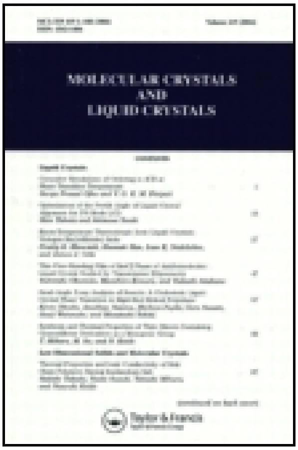


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Some Static Aspects of Molecular Self-Organization from Single Crystal Structural Data

Hans Bock [a]

[a] University of Frankfurt, Niederurseler Hang, Germany, 60439

To cite this article: Hans Bock (1994): Some Static Aspects of Molecular Self-Organization from Single Crystal Structural Data, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 240:1, 155-168

To link to this article: http://dx.doi.org/10.1080/10587259408029726

Mol. Cryst. Liq. Cryst. 1994, Vol. 240, pp. 155–168
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SOME STATIC ASPECTS OF MOLECULAR SELF-ORGANIZATION FROM SINGLE CRYSTAL STRUCTURAL DATA

HANS BOCK
University of Frankfurt, Niederurseler Hang, Germany 60439

Abstract. Compounds are designed and single crystals are grown to study cation solvation phenomena, hydrogen bridge bonding, charge transfer and van der Waals interactions.

THE MOLECULAR STATE APPROACH TO DESIGN CRYSTALS OF ORGANIC COMPOUNDS

Within the time domain of dynamic relaxation, the structure of a molecule can change considerably with its energy and, above all, with the number of its electrons.[1,2] Charges, generated by redox reactions, often inflict severe distortions such as the twisting of the molecular halves in ethylene dianions and dications around the central CC axis, which simultaneously stretches from a C=C double to a C-C single bond [2] (Figure 1).

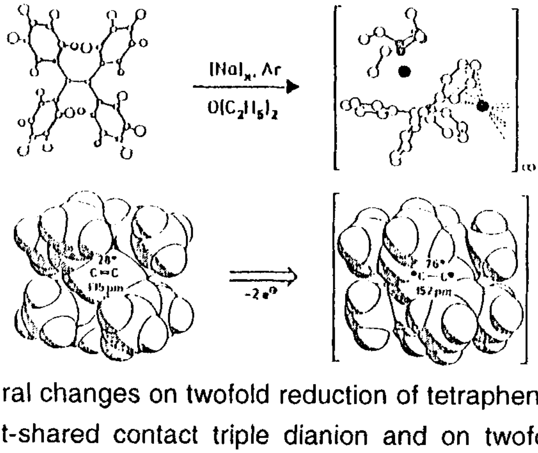


FIGURE 1 Structural changes on twofold reduction of tetraphenylethylene to its solvent-shared contact triple dianion and on twofold oxidation of tetrakis(dimethylamino)ethylene to its dication.[2]

All of these structural changes - including also those due to spatial overcrowding[2] within molecules - nowadays can be predicted either from relevant molecular state measurement data or by approximate energy hypersurface calculations, thereby increasing the hit rate of targeted synthesis efforts and consecutive, often laborious attempts to grow single crystals from aprotic solutions ($c_{H^{\oplus}} < 1$ ppm) under argon.[2]

Altogether, molecular crystals contain organic compounds in their respective ground state close to or even in their global energy minima and with largely "frozen" molecular dynamics. An analysis of crystal lattices, therefore, not only provides an advantageous starting point for the discussion of numerous molecular properties and their quantum chemical calculation, but moreover can yield some static aspects of molecular self-organization.[3]

CATION SOLVATION

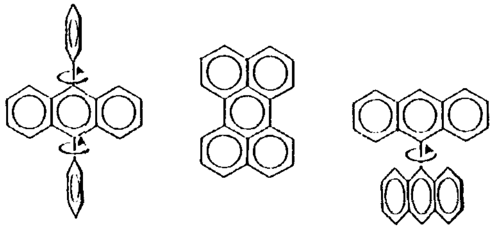
The thermodynamically favourable wrapping of cations by suitable solvent molecules is of essential importance for numerous processes from geology to biology, because the multidimensional networks e.g. of electron transfer, contact ion pair formation and cluster aggregation reactions are all decisively affected by solvation.[2]

To study the respective phenomena in more detail, we have selected alkali metal cations, especially $Na^{\oplus}$ and developed the following preparative method to crystallize from aprotic ether solutions molecular salts, which contain cationic species $[Met^{\oplus}(OR_2)_n]$ optimally solvated (Figure 2: A) under the redox conditions chosen:

$$M + e^{\ominus} \rightleftharpoons [M^{\bullet\ominus}]$$

$$[Met]_{\infty} + m\ \mathrm{Solvent} \underset{(\leftarrow)}{\longrightarrow} [Met^{\oplus}(\mathrm{Solvent})_m] + e^{\ominus}$$

$[M^{\bullet\ominus}]$:



(1)

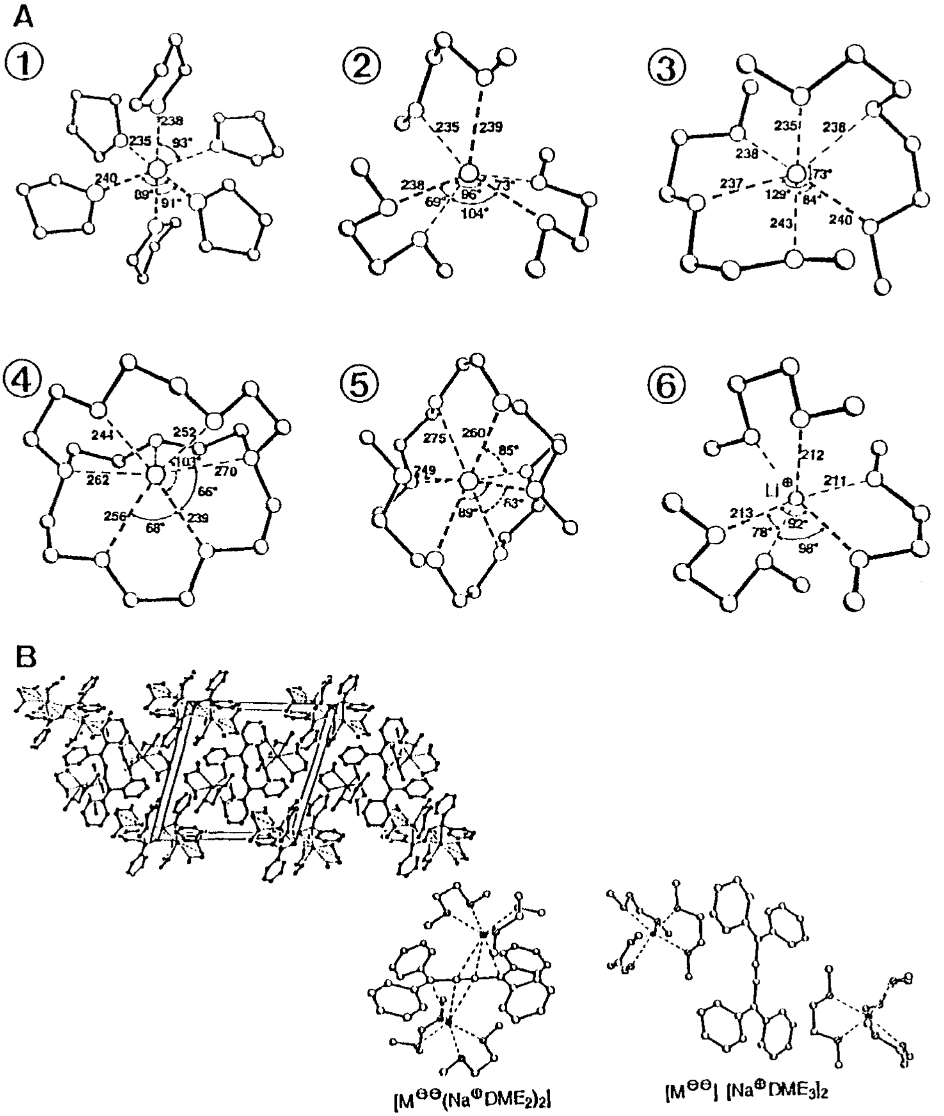


FIGURE 2 (A) Single crystal structures of $Na^{\oplus}$ and $Li^{\oplus}$ counter cations solvated by different ethers (1 $[Na^{\oplus}(THF)_6]$, 2 $[Na^{\oplus}(DME)_3]$, 3 $[Na^{\oplus}(diglyme)_2]$, 4 $[Na^{\oplus}(2.2.2.cryptand)]$, 5 $[Na^{\oplus}(triglyme)_2]$, 6 $[Li^{\oplus}(DME)_3]$) in radical anion salts.[3] (B) Unit cell of tetraphenylbutadiene disodium dimethoxyethane, containing in a 1:1 stoichiometric ratio both the solvent-shared contact ion triple $[M^{\ominus\ominus}(Na^{\oplus}(DME)_2)_2]$ and the solvent-separated ion triple $[M^{\ominus\ominus}][Na^{\oplus}(DME)_3]_2$.[4]

Obviously, one-electron reduction of large π-hydrocarbons such as 9,10-diphenylanthracene, bianthryl or perylene yields radical anions, which due to extensive delocalization of the π-charge no longer possess centers of high electron density well-suited for contact ion pair formation and, therefore, crystallize as separated entities (Figure 2: B).

Based on the structural data, a quasi-isodesmic approximation $[Met^{\oplus}(O_nR_2)_m]_{crystal} \leftrightarrow (Met^{\oplus}) + [(O_nR_2)_m]_{crystal}$, allows a quantum chemical estimate of the enthalpy differences due to solvation:[3] The values $\Delta\Delta H_f^{MNDO}$ calculated e.g. for $[Na^{\oplus}(DME)_3]$, $[Li^{\oplus}DME)_3]$ or $[Na^{\oplus}(THF)_6]$ (Figure 2: 2, 6 and 3) of - 671, -250 or -587 kJ mole^{-1} suggest considerable repulsions within the solvent-shell, which increase both with decreasing cation radius ($Na^{\oplus} \rightarrow Li^{\oplus}$) and with steric overcrowding (DME → THF).

The air- and moisture-sensitive alkaliorganic salts are worth the efforts for their crystallization and structure determination. Thus the serendipitous discovery[4] of both a solvent-shared contact ion triple $[M^{\ominus\ominus}(Na^{\oplus}(DME)_2)_2]$ and a solvent-separated ion triple $[M^{\ominus\ominus}][Na^{\oplus}(DME)_3]_2$ within the same single crystal in a 1:1 stoichiometric ratio (Figure 2: B) suggests inter alia that the $Na^{\oplus}$ solvation by either the tetraphenylbutadiene dianion or by one dimethoxyethane should be of comparable order of magnitude. The above as well as many other examples[2] demonstrate that the molecular information on cation solvation from structural data provides insight in numerous, otherwise hardly accessible facets.

HYDROGEN BRIDGES

Despite of well over 10000 entries in the Cambridge Structural Data Base, still numerous novel aspects of hydrogen bonding in single crystals of main group element molecules are discovered world-wide.

Studies of the Frankfurt group comprise both new preparative methods, aimed especially at hitherto unknown hydrogen bridged molecular aggregates as well as potential calculations, predominantly to evaluate cooperative effects (cf. chapter on polymorphs and isomorphs). Our first contribution[6] reported on the "chemical mimesis" (safety attire of animals to adapt in color and/or shape to their environment) of tetra(2-pyridine)pyrazine dication on replacement of the topotactive $H^{\oplus}$ bridge acceptors $Cl^{\ominus}$ by non-protonable tetraphenyl borate anions (Figure 3).

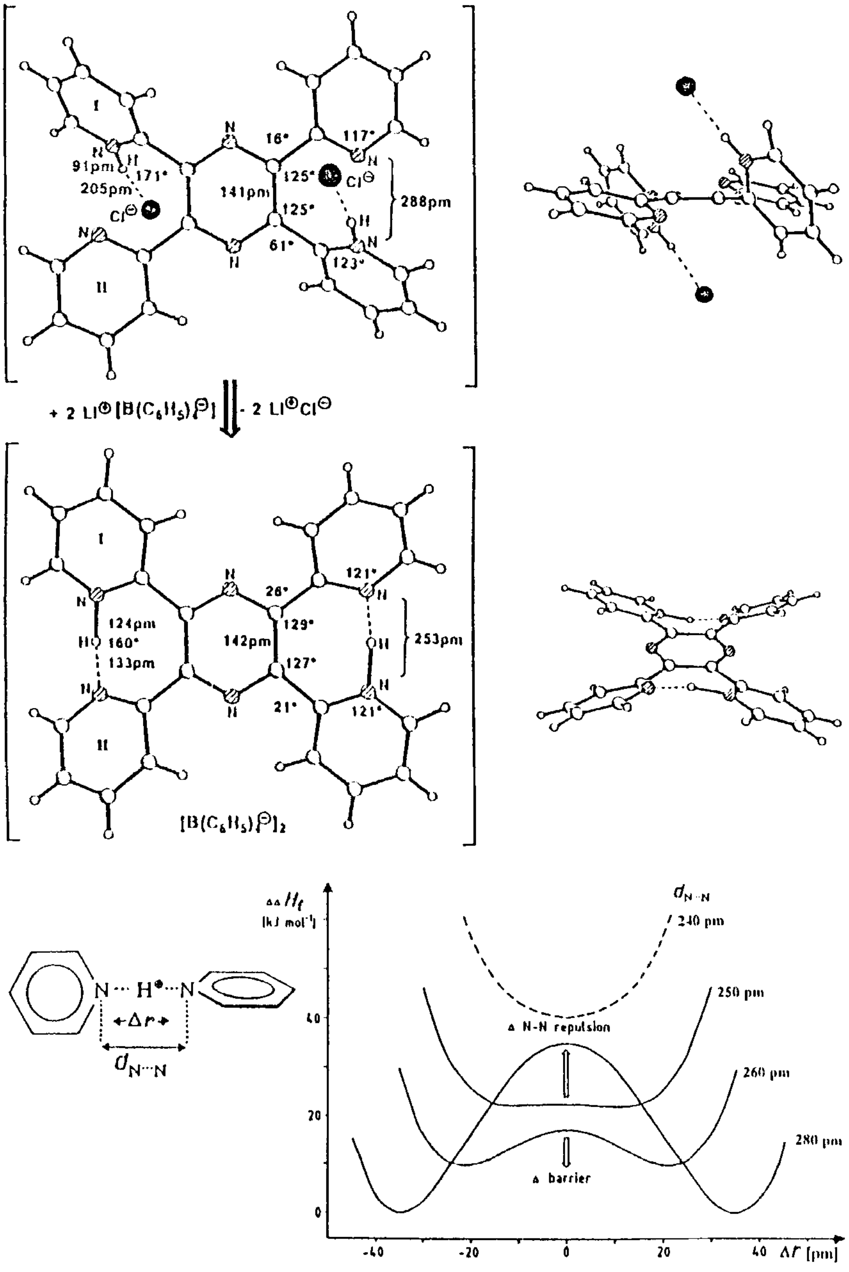
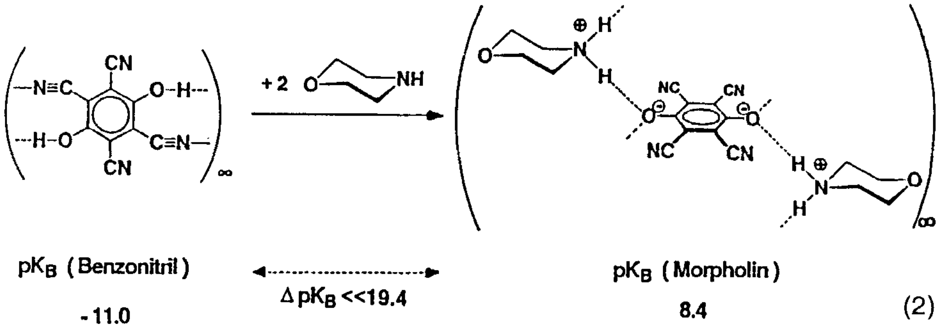


Figure 3 Structures of diprotonated tetra(2-pyridine)pyrazine salts with chloride and non-protonable tetraphenylborate anions as well as semiempirical potential curves for pyridinium pyridine, the hydrogen bridged subunit. 6

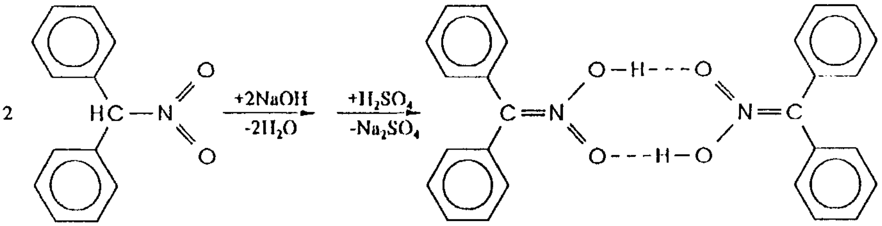
On intramolecular H bridge flattening, the dication turns yellow. To elaborate on the extremely short and almost symmetric N···H···N bond, distance-dependent potential calculations have been performed based on the known neutron diffraction data of 4-aminopyridine perchlorate: for its N···N distance of 270 pm a double minimum results, whereas for the 253 pm determined in the twofold H-bridged tetra(2-pyridine)pyrazine a close to single potential is predicted, in which the proton at room temperature should oscillate with a frequency of about 10^{-9} sec.

Cooperative effects have been investigated repeatedly: For instance, in tetracyanohydroquinone polymer with $(OH\cdots NC)_2$ double bridges, quantum chemical model calculations predict an approximately 10 % increase relative to two $(OH\cdots NC)_1$ single interactions.[7] The polymer can be converted with considerable structural reorganization into a charge-polarized one by recrystallization in the presence of morpholine, a 20 orders of magnitude stronger base:



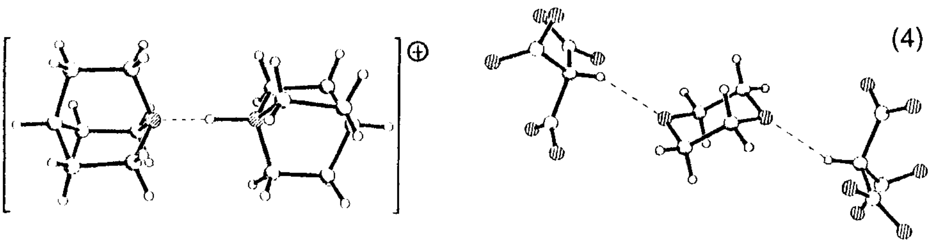
(2)

Due to the additional coulombic interactions, the cooperative effect increases to about 32 %. The largest difference between monomeric and dimeric H bridges $(E\cdots H\cdots E)_{n=1,2}$ predicted by PM3 calculations based on structural data amounts to about 40 % in the novel aci-diphenylnitromethane dimer: [8]



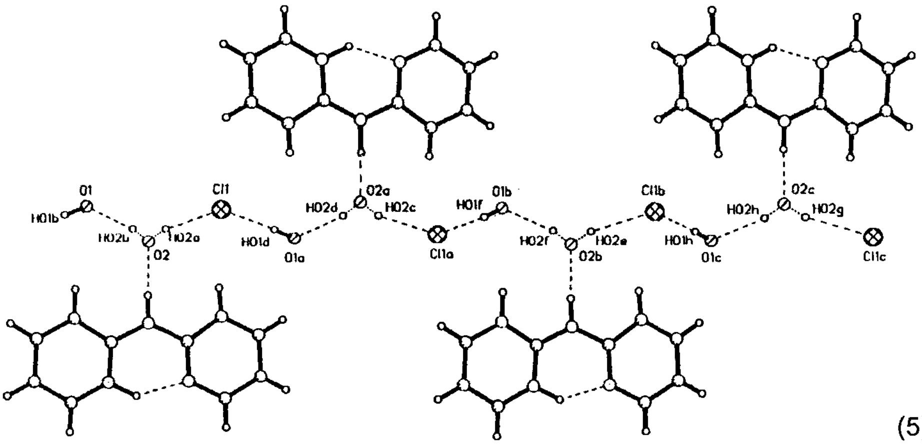
(3)

The crystal growth of H bridged aggregates either from solution by using non-protonable anions or from the gasphase by short-pathway sublimation provides access to amusing prototype structures such as the quinuclidin quinuclidinium tetraphenylborate or the trinitromethane dioxane adduct:[8]



(4)

The rather acidic $(O_2N_3)CH$ forms the shortest hydrocarbon CH···O bridge of only 294 pm length so far registered on the CSD base. The largest H-bonded molecular aggregate crystallized up to now in Frankfurt is dipyridineamine hydrochloride dihydrate: [9]



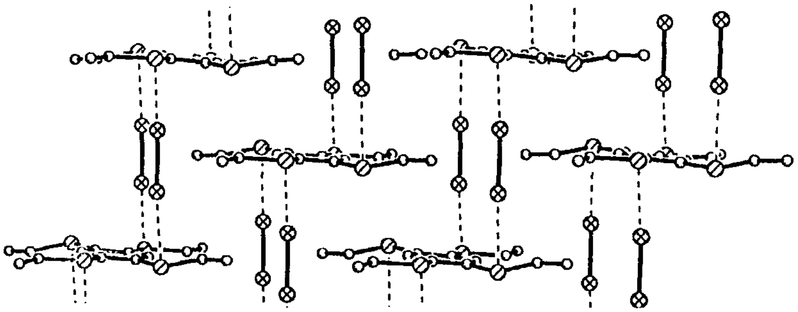
(5)

Its two dimensional $(HOH\cdots Cl^{\ominus}\cdots HOH\cdots HOH)_{\infty}$ layer is anchored at the staples of dipyridiniumamine cations. In addition, charge transfer complexes as well as polymorphs and isomorphs have been structurally characterized, which contain as a well-established dominant packing motif H bridge dimers.[9]

CHARGE TRANSFER

This most recent one of our research projects aims at single crystal growth of complexes, in which donor and acceptor components are not stacked in different staples but rather interact with each other in stoichiometric ratios. From the so far structurally characterized compounds each one σ- and one π-type example will be presented.

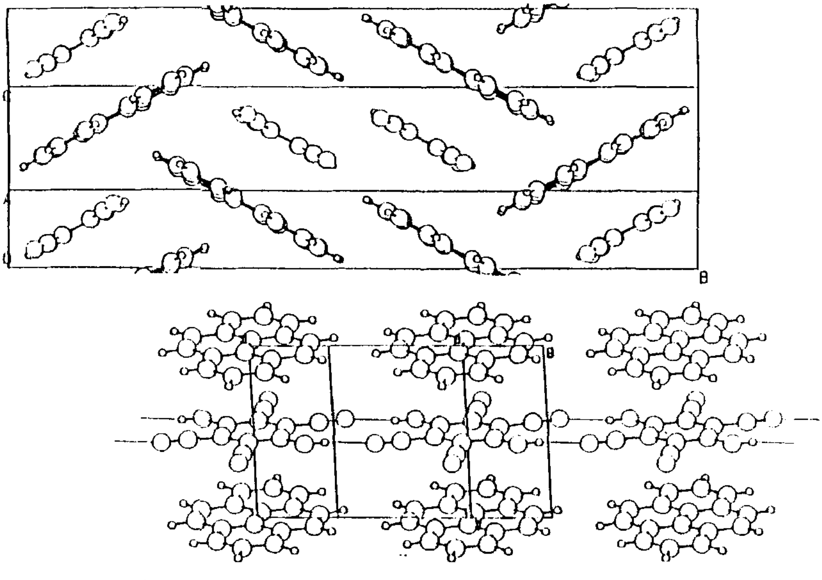
Cooling of a tetrachloromethane solution containing 1,2,3,5-tetra(thioethyl)benzene and bromine in 1:2 ratio produces black blocks, which surprisingly consist of tetrathiobenzene layers interconnected alternatingly by bromine sticks:[10]



(6)

Relative to Br_2 molecules in the gasphase, the distance Br-Br is elongated from 227 to 240 pm, substantiating the charge transfer S → Br from the sulfur donor centers.

π-Donor/acceptor complexes exhibiting a partly herringbone-like packing motif such as pyrene/tetracyanobenzene: [10]

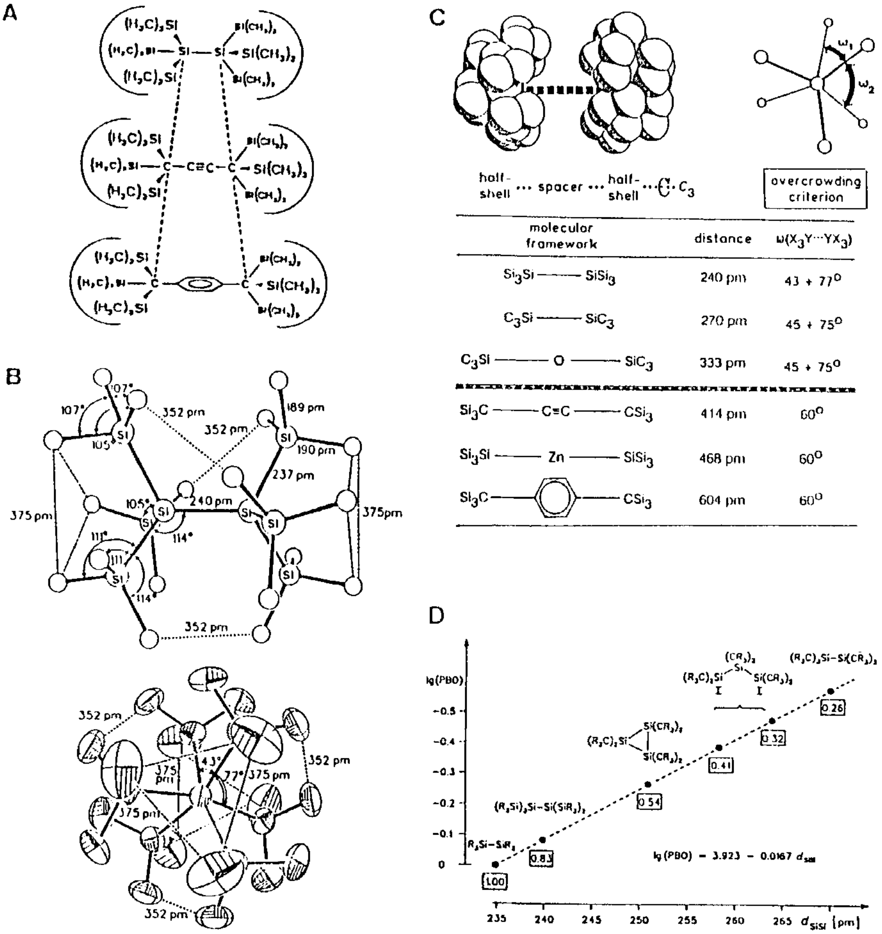


(7)

can be levelled out by superimposing an H bridge dimer interaction via exchange of the tetracyanobenzene for the corresponding hydroquinone acceptor[10] (see (2)).

VAN DER WAALS INTERACTIONS

Bulky tris(trimethylsilyl)silyl and tris(trimethylsilyl)methyl substituents are well-suited to design model compounds with spacers of different lengths between the half-shells (Figure 4: A), which allow to study intramolecular van der Waals interactions (Figure 4: B).[11]



molecular framework	distance	$\omega(X_3Y \cdots YX_3)$
Si_3Si —— $SiSi_3$	240 pm	43 + 77°
C_3Si —— SiC_3	270 pm	45 + 75°
C_3Si —— O —— SiC_3	333 pm	45 + 75°
Si_3C —— C≡C —— CSi_3	414 pm	60°
Si_3Si —— Zn —— $SiSi_3$	468 pm	60°
Si_3C —— ⌬ —— CSi_3	604 pm	60°

FIGURE 4. (A) Organosilicon model compounds with spacers of different lengths between bulky substituent half-shells. (B) Single crystal structure of hexakis(trimethylsilyl)disilane.[11] (C) Dihedral angle overcrowded-ness criterion for half-shell/spacer model compounds of local C_3 symmetry. (D) Pauling bond order/SiSi bond lengths correlation suggesting additional van der Waals attraction in the hydrocarbon skin of overcrowded organosilicon molecules.[11]

In hexakis(trimethylsilyl)disilane (Fig. 4: B), the two half-shells of the space-filling substituents $Si[Si(CH_3)_3]_3$ are connected by a Si-Si bond elongated to 240 pm. Some of the C···C distances between the two molecular halves amount to only 352 pm; that is, they are shortened by 12 % relative to the sum of the van der Waals radii of two methyl groups, which are usually considered to be each about 200 pm.[2] The molecular skeleton Si_3Si-$SiSi_3$ of D_3 symmetry unexpectedly exhibits two different dihedral angles of 43^{o} and 77^{o} (Fig. 4: B and C). Structural comparison with analogous molecules (Fig. 4: C) reveals that the dihedral angles ϖ_1 and ϖ_2 between the spacer-linked substituents are different if these are less than 333 pm apart, but identical if more than 414 pm apart. The twisting $D_{3d} \rightarrow D_3$ of the molecular skeletons from the optimal conformation with $\varpi(X_3Y\text{-}YX_3) = 60^{o}$ is therefore an appropriate criterion for steric overcrowding, which leads to extremely short C···C van der Waals distances between some of the methyl groups (Fig. 1: B) as a result of their additional cogwheel-meshing in the interior of the molecule.

Spatial overcrowding especially due to tris(tert-butyl)silyl substituents (Fig. 4: C) *with C-C distances, which are approximately 40 pm shorter than the C-Si* ones, stretches the standard Si-Si bond length of 235 pm in hexamethyldisilane to 270 pm and lowers the corresponding Pauling bond order from 1.0 to 0.26. It has been proposed, therefore, that the (in some cases extremely) weakened central Si-Si bonds are strengthened by additional attractive van der Waals interactions in the enveloping hydrocarbon "skin". This assumption would also be compatible with the structure of hexakis(trimethylsilyl)disilane, in which some of the intramolecular C···C distances only amount to 352 pm (Fig. 4: B), and also with intermolecular distances found on lattice packing analysis. The pronounced van der Waals interactions in and between organosilicon molecules presumably are due to the rather strong polarization $Si^{\delta\oplus}$-$C^{\delta\ominus}$-$H^{\delta\oplus}$ caused by the low effective nuclear charge of Si centers.[12]

POLYMORPHS AND ISOMORPHS

In general, the structures of polymorphic conformers of the very same molecule as well as the almost identical isomorphic crystals of chemically related and only slightly differing compounds provide multi-faceted information on weak interactions in and between ensembles in crystals. Polymorphism is widely documented in the literature.[13]

For both poly- and isomorphism each one example from the Frankfurt Group will be presented here. Tetraisopropyl-p-phenylene diamine crystallizes in monoclinic and triclinic modifications[13] (Fig. 5), in which the nitrogen lone pairs are either perpendicular to or in the benzene ring plane.

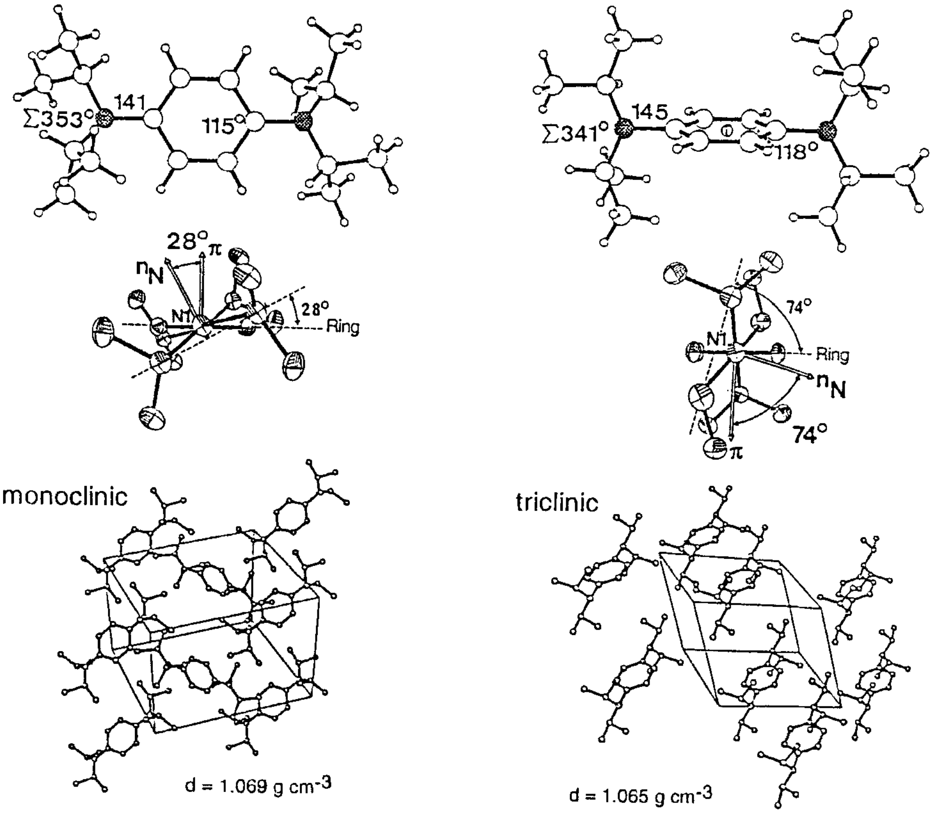
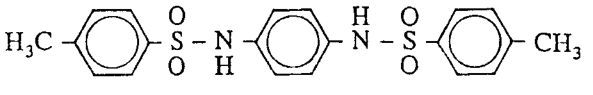


FIGURE 5. Single crystal structures at 150 K of monoclinic and triclinic tetraisopropyl-p-phenylene diamine.

Extensive hypersurface calculations starting from the structural data yield comparable enthalpies of formation for both conformers, in which n_N/π delocalization and H/H repulsions especially with the ring-ortho-hydrogens counteract. Despite of the only small differences in the densities, the one of the monoclinic modification obtained by very slow sublimation is slightly higher. Crystal lattice energy calculations also predict the triclinic modification, which rapidly crystallizes from a saturated hydrocarbon solution, to be the less stable one.

To further explore potential p-phenylene diamine polymorphs, derivatives with different alkyl groups at each N center are synthesized via the ditosyl intermediate.[14] Its purifications by recrystallization from solvents such as acetone or tetrahydrofurane, unexpectedly led to the discovery of isotypic lattices, which are dominated by an H bridge dimer (NH···O(S))$_2$ packing motif (Fig. 6).



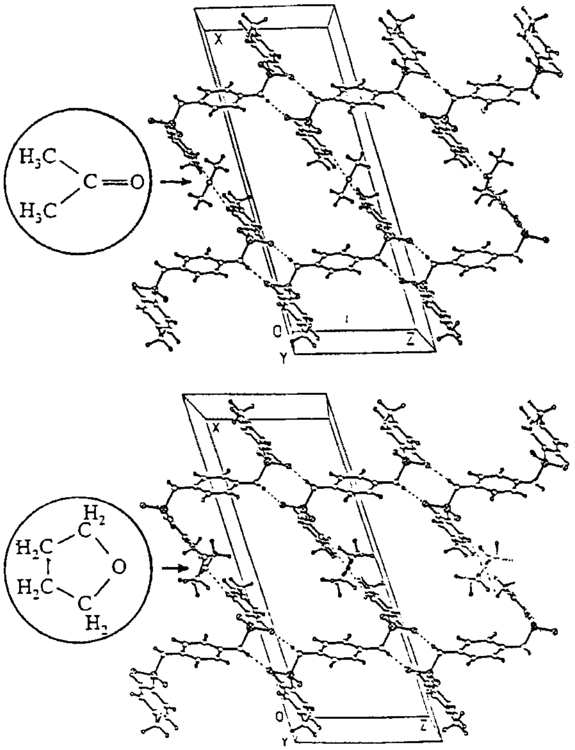


FIGURE 6 Single crystal structures of N,N'-ditosyl-p-phenylene diamine acetone and tetrahydrofurane (space group C2/c, axes a = 2446,2 and 2409,7, b = 1077,9 and 1100,7, c = 938,6 and 943,5 pm).

Preliminary NMR data allow to conclude that the inclusion of the different solvents should produce isomorphs. On recrystallization from pyramidal dimethylsulfoxide, the H bridge dimer is converted to a double (NH···OS(CH$_3$)$_2$) adduct.[14]

CRYSTALLIZATION - FASCINATION

This interim research report covers two years of fascination by structures of charge-perturbed and sterically overcrowded molecules,[2] and another year of increasing packing-mindedness. Starting from preceding investigations in the gasphase on short-lived molecules and in solution on paramagnetic species, both experience in relevant measurement methods such as photoelectron or ESR/ENDOR spectroscopy and in quantum chemical rationalization of the resulting molecular state data provided useful guidelines for a largely preparative group to learn in addition how to crystallize precalculated distorted molecules and to determine their solid state structures.

Also in the area of lattice packing analysis we are just beginners, grateful for advices of knowledgeable long-time professionals and heavily relying on the wealth of literature as quoted in our publications.[1-14] And, there are increasingly more questions than answer with regard to "what crystallizes how and why?" or, put positively, there is a lot of stimulation for numerous future experiments.

Acknowledgements. Above all, the achievements of dedicated coworkers are specified as follows: structure determination C. Näther, K. Ruppert and H. Schödel, quantum chemical calculations Z. Havlas and J. Vondrasek, alkali-organic compounds C. Arad, T. Hauck, A. John, C. Näther, S. Nick and K. Ruppert, hydrogen bridges R. Dienelt, M. Gluth, N. Nagel, H. Schödel, W. Seitz, T. Van and T. Vaupel, charge transfer complexes I. Göbel, A. Rauschenbach, W. Seitz, M. Sievert and K. Ziemer, van der Waals interactions I. Göbel and J. Meuret, polymorphs and isomorphs I. Göbel, A. John, C. Näther, N. Nagel and H. Schödel. Diffractometer measurement time was generously provided by R. Schlögl (Frankfurt) and W.A. Herrmann (Munich). Advices for structural solutions from J.W. Bats and W. Bensch (Frankfurt) as well as K. Herdtweck (Munich) are appreciated. Last, but not least we thank A Gavezotti and G. Fillipini (Milano) for their cooperation. Our research has been generously supported by the Deutsche Forschungsemeinschaft, the State of Hesse, Fonds der Chemischen Industrie as well as the M. Buchner, A. v. Humboldt (Z.H.) and A. Messer-Foundations.

REFERENCES

1. H. Bock "Molecular States and Molecular Orbitals" Angew. Chem., 89, 631 (1977); Angew. Chem. Int. Ed. Engl. 16, 613 (1977) and lit. cit.
2. H. Bock, K. Ruppert, C. Näther, Z. Havlas, H.-F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel and B. Solouki "Distorted Molecules: Perturbation Design, Preparation and Structures", Angew. Chem., 104, 564 (1992); Angew. Chem. Int. Ed. Engl., 31, 550 (1992) and lit. cit.
3. H. Bock, "Crystallisation as a Model for Molecular Self-Organization?", Annals 1992 of the German Academy of Natural Scientists Leopoldina, 38, 221 (1993) and lit. cit.
4. H. Bock, C. Näther, K. Ruppert and Z. Havlas, J. Am. Chem. Soc., 114, 6907 (1992).
5. H. Bock, C. Näther, Z. Havlas, A. John and C. Arad, unpublished results, cf. H. Bock, A. John, C. Näther, Z. Havlas and E. Mihokova, Helv. Chim. Acta 1993, in print.
6. H. Bock, T. Vaupel, C. Näther, K. Ruppert and Z. Havlas, Angew. Chem., 104, 348 (1992); Angew. Chem. Int. Ed. Engl., 31, 299 (1992) and lit. cit.
7. H. Bock, W. Seitz, Z. Havlas and J.W. Bats, Angew. Chem., 105, 410 (1993); Angew. Chem. Int. Ed. Engl., 32, 411 (1993).
8. H. Bock, R. Dienelt, H. Schödel, Z. Havlas, E. Herdtweck and W.A. Herrmann, Angew. Chem., 105 (1993), in print, Angew. Chem. Int. Ed. Engl., 32 (1993) in print.
9. H. Bock, C. Näther, H. Schödel, T. Vaupel, R. Dienelt, M. Gluth, S. Nick, T. Van, Z. Havlas, J. Vondrasek, unpublished results.
10. H. Bock, C. Näther, J.W. Bats, Z. Havlas, A. Rauschenbach, W. Seitz,. I. Göbel, T. Hauck, M. Sievert, K. Ziemer, recent results.
11. H. Bock, J. Meuret and K. Ruppert, Angew. Chem., 105, 413 (1993), Angew. Chem. Int. Ed. Engl., 32, 415 (1993) as well as J. Organomet. Chem., 445; 19 (1993) and lit. cit.
12. H. Bock "Molecular States of Silicon-Containing Compounds" Angew. Chem., 101, 1659 (1989); Angew. Chem. Int. Ed. Engl., 28, 1627 (1989).
13. H. Bock, I. Göbel, C. Näther, Z. Havlas, A. Gavezotti, G. Filippini, Angew. Chem. 105 (1993), in print, Angew. Chem. Int. Ed. Engl., 32 (1993), in print, and lit. cit.
14. H. Bock, C. Näther, N. Nagel, H. Schödel, recent results.